

PRECIPITATION AND REACTION PRODUCTS OF FLUIDS IN MARTIAN ORTHOPYROXENITE ALH84001.

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Introduction. The ALH84001 meteorite was classified as a cumulate orthopyroxenite of martian origin [1]. In contrast to other SNC meteorites, ALH84001 contains abundant Fe-Mg carbonates, which give strong evidence for hydrothermal or fluid activities on Mars [1-3]. Recently, PAHs, carbonate globules, and some associated secondary minerals were described on fresh fracture surface of that meteorite and the findings were considered as possible remains of ancient martian biota [4]. The purpose of this work is to study the genesis of minor phases in order to learn more about fluid activities in this meteorite.

Methods. We have studied polished thin section ALH84001,141 by optical microscopy, analytical scanning electron microscopy, and electron probe microanalysis, following standard procedures.

Results. ALH84001 is an orthopyroxenite breccia, which is composed of clasts and a crushed, recrystallized, and lithified matrix. The clasts are up to a few mm in size and consist exclusively of orthopyroxene grains. Minor constituents and accessories are chromite, feldspar-rich glass, augite, olivine, Ca-phosphate, carbonate, a silica phase, Fe-sulfides, and Fe-sulfates. Chromite is present in three different sizes. Large grains (up to 0.5 mm size) are equidimensional and strongly birefringent. They occur within and in between orthopyroxenes and are usually accompanied by aggregates of smaller chromites (up to about 50 μm in diameter) and by feldspar-rich glass (Fig. 1). Aggregates of the smaller chromites commonly fill veins where they are associated also with feldspar-rich glass, silica, and Fe-sulfides (pyrrhotite and pyrite). Very small chromites ($\pm 1 \mu\text{m}$) are disseminated throughout the orthopyroxenes and carbonates (Fig. 2). Feldspar-rich glass also fills veins and pockets (some of which are surrounded by radiating cracks), where it is associated with sulfides, silica, and olivine. Silica and olivine also occur as small (10 μm) inclusions in orthopyroxene. A small angular pocket (40x90 μm) was found within a large orthopyroxene grain which consists mainly of feldspar-rich glass and silica with minor olivine, enveloped by feldspar, and Ca-phosphate.

The breccia matrix is fine-grained (10-30 μm grain size) granular and shows a banded texture. Orthopyroxene dominates the matrix, but it appears to be somewhat enriched in chromite and feldspar-rich glass as compared to the coarse-grained clasts. Glass and chromite fill complex wavy veins. Carbonates are also more abundant in the matrix as compared to the clasts and occur as patches of interlocked grains in between orthopyroxenes or fill cavities or short veins (Fig. 2). They commonly contain small chromites, Fe-sulfides, and Fe-sulphates, and are associated with envelopes rich in sub- μm Fe oxides and sulfides, which separate the common carbonate from magnesite and which in places show a rhythmic banding parallel to that interface (Fig. 3).

Averaged analyses of orthopyroxene, augite, and chromite, as well as single analyses of olivine, feldspar-rich glass, and silica are given in the Table. Most phases have fairly homogeneous compositions, except for glass and carbonates. Glass has a feldspar-like composition, mostly poor in K and non-stoichiometric, but K-rich glasses are also present (Fig. 4). Chromite contains 5.5 wt.% of Fe_2O_3 that probably causes the birefringence [5]. Carbonates vary compositionally (Fig. 5) along their intergranular extension and along veins from $\text{Cc}_2\text{Mg}_{73}\text{Sd}_{25}$ to $\text{Cc}_{17}\text{Mg}_{46}\text{Sd}_{37}$ and to pure magnesite ($\text{Cc}_5\text{Mg}_{92}\text{Sd}_3$) with a correlated decrease of the Mn content. Ankeritic compositions of about $\text{Cc}_{34}\text{Mg}_{37}\text{Sd}_{29}$ are rare.

Discussion. Our mineral compositions are very similar to those found earlier [1-4,6-7], and support the conclusion that ALH84001 is a homogeneous cumulate rock. However, textural relationships, mineral associations, and chemical composition of minor phases suggest an unusually complex history of ALH84001. Fluids, as noted earlier [7-10], seem to have been active under a variety of conditions. Silicate melt and CO_2 -rich aqueous fluids have been made responsible for the formation of maskelynite, apatite, and carbonate [8, 10]. Our observations support this view, but in addition force us to make some modifications to this model. From textural relationships we have to suspect that fluids precipitated chromite (which fills pockets and odd-shaped veins), sulfides, the feldspar-like glass, phosphates, free silica, sulfates, and some of the carbonates. This view is supported by trace element abundances in minerals and the bulk [8, 10,11].

Of the abundant carbonates in ALH84001 only a small proportion appears to have been precipitated from a fluid (the vein carbonates). Most of the carbonates replace a preexisting phase. This replacement is not accompanied by compositional changes of associated silicates, which suggests that they were formed by a dry CO_2 -rich fluid (which was rich in Ca and in trace elements). The similarity of the Mg/Fe ratios of some carbonates and the major silicates (Fig.5) supports that view. Redox conditions were apparently changing from oxidizing to strongly oxidizing, leading to the replacement of Mg-Fe carbonates by magnesite covered by a rhythmic, diffusion-controlled, precipitation front containing the expelled Fe as Fe_3O_4 , FeS_2 , and Fe sulfate in places. The morphology of magnetites in that zone (rods, ribbons, platelets) indicates growth from a fluid or dilute solution [12].

The non-stoichiometrical and in places very K-rich composition of feldspar-like glasses creates some problems if it is related to a newly discovered high pressure phase [13] from the Peace River and Tenham chondrites. The K-poor and the K-rich glasses have both a 5/10 cation/oxygen ratio, which is similar to that found in the high pressure phase. Radial cracks around some of the glass pockets support this interpretation.

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Table. Mineral Chemistry.

	Opx		Cpx		Olivine		Glass		Chromite		Silica
	n=19	$\pm 1\sigma$	n=12	$\pm 1\sigma$					n=24	$\pm 1\sigma$	
SiO ₂	53.1	0.8	54.2	0.4	37.4	36.6	60.8	64.3	0.05	0.03	96.7
TiO ₂	0.16	0.02	0.35	0.09			0.06	0.04	2.17	0.36	
Al ₂ O ₃	0.61	0.08	1.38	0.20	0.36		26.8	22.20	7.95	0.51	0.45
Cr ₂ O ₃	0.33	0.06	0.77	0.08	0.03	0.02		0.02	49.1	2.4	
Fe ₂ O ₃										5.47	1.19
FeO	17.4	0.4	7.90	0.33	28.0	29.0	0.25	0.23	28.3	0.4	0.24
MnO	0.47	0.04	0.28	0.02	0.5	0.43			0.28	0.05	
MgO	25.3	0.5	15.6	0.14	32.5	32.3	0.02		3.72	0.19	
CaO	1.58	0.10	20.1	0.3	0.14	0.07	7.4	2.68			0.07
Na ₂ O	0.03	0.01	0.42	0.02	0.10		3.96	3.70			0.13
K ₂ O							0.40	3.50			0.03
Sum	98.98		101.0		99.03	98.42	99.69	96.67	97.04		97.62
mg#	72.2		77.9		67.4	66.5			19.0		

Fe₂O₃ calculated assuming stoichiometry**Figures:**

Figure 1. Large chromite (light grey) associated with granular chromite and feldspar-rich glass (dark grey). Smaller size chromite also fills veins, as does the glass. BSE image.

Figure 2. Mg-Fe-Ca carbonate (dark grey) replaces former silicate grains and fills cavities (Mg-rich, very dark grey). Note the distribution of very small chromites in orthopyroxene (grey) and carbonate. BSE image.

Figure 3. Oxide- and sulfide-rich interface between magnesite (dark grey) and Mg-Fe-Ca carbonate (grey) surrounded by orthopyroxenes (light grey). BSE image.

Figure 4. Molecular projection of feldspar-rich glass compositions in ALH84001.

Figure 5. Carbonate compositions in ALH84001. Note the magnesite cluster and the Mg-poor composition of the oxide- and sulfide-rich bands separating magnesite from the common carbonates. Note also the overlap in carbonate composition with those of orthopyroxene and olivine.

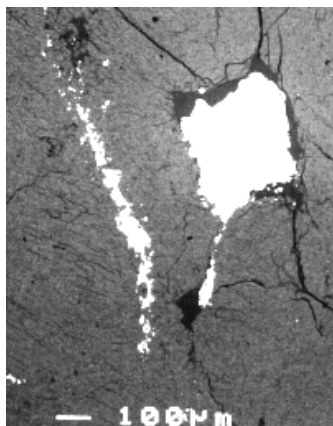


Fig. 1

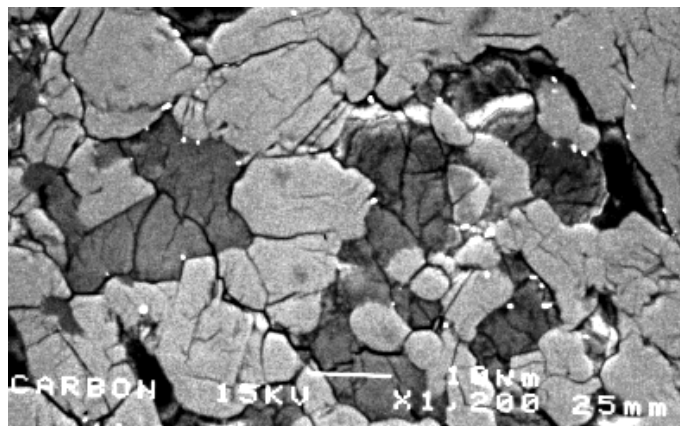


Fig. 2



Fig. 3

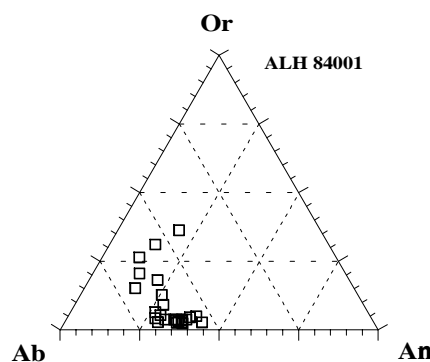


Fig. 4

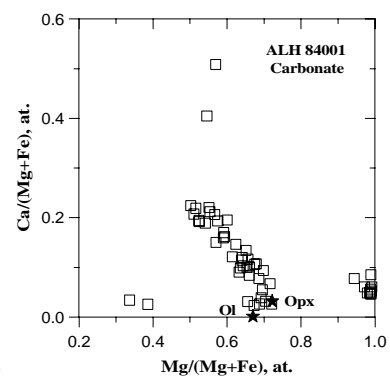


Fig. 5